

FORM PTO-1390
(REV. 11-1-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

06-01US

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

09/889368

INTERNATIONAL APPLICATION NO.
PCT/DE00/00065

INTERNATIONAL FILING DATE
1/7/2000

PRIORITY DATE CLAIMED
1/12/1999

TITLE OF INVENTION

MALATYL POLYSACCHARIDES, THEIR PRODUCTION AND THEIR USE

APPLICANT(S) FOR DO/EO/US

Waldemar Lazik

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31)
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau)
 - b. ☒ has been communicated by the International Bureau
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is attached hereto
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4)
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau)
 - b. ☐ have been communicated by the International Bureau
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired
 - d. ☐ have not been made and will not be made
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3))
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
The declaration is a true and exact copy of the original.
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5))

Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included
13. ☒ A **FIRST** preliminary amendment
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment
15. ☐ A substitute specification
16. ☐ A change of power of attorney and/or address letter
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter 2 and 35 U.S.C. 1.821 - 1.825
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4)
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4)
20. ☒ Other items or information:
Application Data Sheet

"Express Mail" Label # EF 419 679 020 US - I hereby certify that this paper or fee is being deposited with the USPS "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on 07/12/2001, and is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.

Gudrun E. Hockett, Patent Agent

U.S. APPLICATION NO. (if known, see 37 CFR 1.53)

INTERNATIONAL APPLICATION NO.
PCT/DE00/00065

ATTORNEY'S DOCKET NUMBER
06-01US

09/889368

21 ☒ The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):

Neither international preliminary examination fee (37 CFR 1.482)
nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO
and International Search Report not prepared by the EPO or JPO **\$1000.00**

International preliminary examination fee (37 CFR 1.482) not paid to
USPTO but International Search Report prepared by the EPO or JPO **\$860.00**

International preliminary examination fee (37 CFR 1.482) not paid to USPTO
but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **\$710.00**

International preliminary examination fee (37 CFR 1.482) paid to USPTO
but all claims did not satisfy provisions of PCT Article 33(1)-(4) **\$690.00**

International preliminary examination fee (37 CFR 1.482) paid to USPTO
and all claims satisfied provisions of PCT Article 33(1)-(4) **\$100.00**

ENTER APPROPRIATE BASIC FEE AMOUNT =

CALCULATIONS PTO USE ONLY

\$ 860.00

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(e))

\$

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
Total claims	10 - 20 =	0	x \$18.00
Independent claims	3 - 3 =	0	x \$80.00
MULTIPLE DEPENDENT CLAIM(S) (if applicable) 0			+ \$270.00

\$

\$

\$

\$

TOTAL OF ABOVE CALCULATIONS =

\$ 860.00

☒ Applicant claims small entity status (See 37 CFR 1.27). The fees indicated above
are reduced by 1/2.

\$ 430.00

+

SUBTOTAL =

\$ 430.00

Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(f)).

\$

TOTAL NATIONAL FEE =

\$ 430.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) **\$40.00** per property +

\$

TOTAL FEES ENCLOSED =

\$ 430.00

Amount to be
refunded:

\$

charged:

\$

a. ☒ A check in the amount of \$ 430.00 to cover the above fees is enclosed (check # 1245)

b. ☐ Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees!
A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
overpayment to Deposit Account No. 50-1199. A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. Credit card
information should not be included on this form. Provide credit card information and authorization on PTO-2038!

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR
1.437 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO

Gudrun E. Hockett, Patent Agent
P.O. Box 3187
Albuquerque, NM 87190-3187

SIGNATURE

Gudrun E. Hockett

NAME

35,747

REGISTRATION NUMBER

12 July 2001

U.S. APPLICATION NO. (if known, see 37 CFR 1.15)		INTERNATIONAL APPLICATION NO. PCT/DE00/00065		ATTORNEY'S DOCKET NUMBER 06-01US	
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21 ☒ The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1000.00

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ENTER APPROPRIATE BASIC FEE AMOUNT =

CALCULATIONS PTO USE ONLY

Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e))				\$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$	
Total claims	10 - 20 =	0	x \$18.00	\$	
Independent claims	3 - 3 =	0	x \$80.00	\$	
MULTIPLE DEPENDENT CLAIM(S) (if applicable) 0				+ \$270.00	\$
TOTAL OF ABOVE CALCULATIONS =				\$ 860.00	
<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				+ \$ 430.00	
SUBTOTAL =				\$ 430.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f))				\$	
TOTAL NATIONAL FEE =				\$ 430.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) \$40.00 per property				+ \$	
TOTAL FEES ENCLOSED =				\$ 430.00	
				Amount to be refunded:	\$
				charged:	\$

a. ☒ A check in the amount of \$ 430.00 to cover the above fees is enclosed (check # 1245)

b. ☐ Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 50-1199. A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.337 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO

Gudrun E. Hockett, Patent Agent
P.O. Box 3187
Albuquerque, NM 87190-3187

Gudrun E. Hockett
SIGNATURE
Gudrun E. Hockett
NAME
35,747
REGISTRATION NUMBER
12 July 2001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

"Express Mail" Mailing Label Number EF 419 679 020 US

Date of Deposit July 12, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.


Gudrun E. Hockett, Patent Agent

Applicant: Waldemar Lazik
Serial No: not yet known (based on PCT/DE00/00065)
International Filing Date: 1/7/2000
U.S. Filed: 7/12/2001
Title: Malatyl Polysaccharides, Their Production and Their Use

**Assistant Commissioner for Patents
Washington, D.C. 20231**

PRELIMINARY AMENDMENT

Prior to the first office action, please amend the instant application as follows:

IN THE SPECIFICATION:

Please substitute pages 1, 2 and 8 on file with the attached clean copies of the amended pages 1, 2, 8. A marked-up version of the pages 1, 2, 8 with all the changes shown is also attached.

IN THE CLAIMS:

Claims 1 through 7 are cancelled.

Please add the attached new claims 8-17 to the specification.

IN THE ABSTRACT:

Please add the attached Abstract of the Disclosure to the specification.

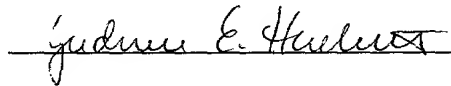
REMARKS

Claims 1 through 7 have been cancelled and replaced with claims 8-17 drafted in proper U.S. format. Proper headings according to the guidelines for drafting a nonprovisional patent application under 35 U.S.C. 111(a) have been added. A proper Abstract of the Disclosure has been added to the specification.

In view of the foregoing, it is submitted that this application is now in condition for allowance and such allowance is respectfully solicited.

Authorization is herewith given to charge any fees or any shortages in any fees required during prosecution of this application and not paid by other means to Patent and Trademark Office deposit account 50-1199.

Respectfully submitted on July 12, 2001



Gudrun E. Hockett, Ph.D.
Registration No. 35,747

Gudrun E. Hockett, Patent Agent
P.O. Box. 3187
Albuquerque, NM 87190-3187

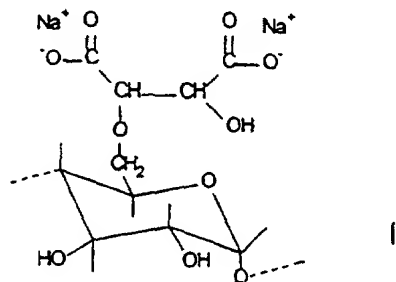
Telephone: (505) 266-2138
Facsimile: (505) 266-2138

GEH/Encl.: pages 1, 2, 8 (clean copies and marked-up versions); claims 8-17; Abstract of the Disclosure

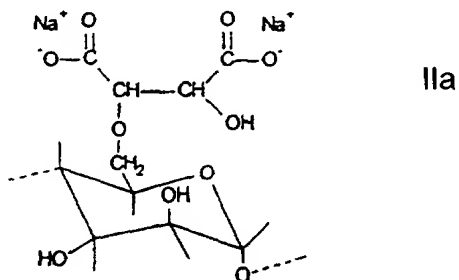
COPY OF NEW CLAIMS 8-17

8. Malatyl polysaccharides prepared by reacting polysaccharides and an epoxy compound selected from the group consisting of cis-epoxy succinate or epoxy carboxylic acids.

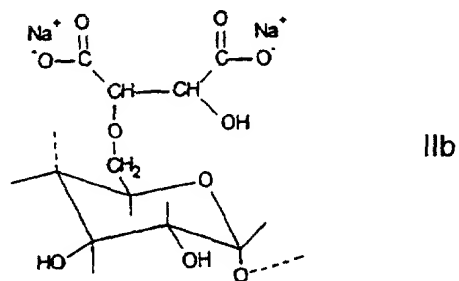
9. A malatyl polysaccharide according to claim 8 in the form of malatyl starch of the general formula (I):



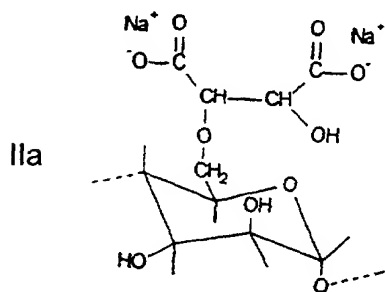
10. A malatyl polysaccharide according to claim 8 in the form of malatyl galactomannan of the general formula (IIa)



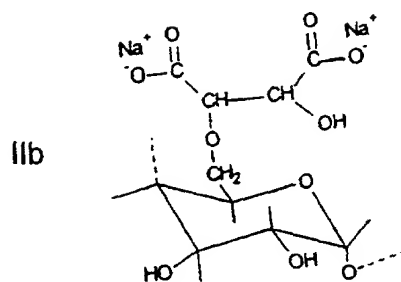
11. A malatyl polysaccharide according to claim 8 in the form of malatyl galactomannan of the general formula (IIb)



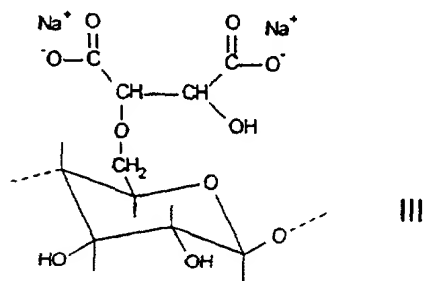
12. A malatyl polysaccharide according to claim 8 in the form of malatyl galactomannan of the general formula (IIa) and (IIb)



and



13. A malatyl polysaccharide according to claim 8 in the form of malatyl cellulose of the general formula (III).



14. A method of preparing malatyl polysaccharides according to claim 1,

comprising the step of:

reacting polysaccharides with an epoxy compound selected from the group consisting of cis-epoxy succinate or analog epoxy carboxylic acids.

15. A method according to claim 14, wherein the epoxy compound is epoxy succinate and the step of reacting is carried out in a suspension.

16. A method according to claim 14, wherein the epoxy compound is epoxy succinate and the step of reacting is carried out in solid phase.

17. A method of using malatyl polysaccharides according to claim 8 as thickening agents or complexing agents for cations or organic compounds or as ion exchangers for aqueous systems or as adjuvants in pharmaceutical applications or as ingredients for hygiene articles.

CLEAN COPY OF PAGE 1

Malatyl Polysaccharides, Their Production and Their Use

Background of the Invention

1. Field of the Invention

The invention relates to malatyl polysaccharides made of polysaccharides and cis-epoxy succinate or other epoxy carboxylic acids, methods for their production as well as their use in detergents, thickening agents, complexing agents for cations or organic compounds or as ion exchangers for aqueous system or as adjuvants in pharmaceutical applications (for example, tablet bursting agents, suspension stabilizes etc.) or as ingredients in hygiene articles and medical fields.

2. Description of the Related Art

In general, reactions of starch or cellulose with epoxides (oxiranes), for example, with ethylene oxide or propylene oxide, to form hydroxyalkyl derivatives have been known for quite some time and have been described in many publications (for example, K. Engelskirchen in "Methoden der organischen Chemie", Vol. E20, p. 2135ff, 1987). Hydroxyalkyl starches or hydroxyalkyl cellulose compounds are non-ionic derivatives which are used often in electrolyte-rich systems, for example, as thickening agents because they react substantially inert in aqueous systems (for example, without viscosity loss) in regard to electrolytes (salts).

Reactions of starch or cellulose to ionic derivatives have also been described often (see, inter alia, R. L. Davidson, Handbook of Water-soluble Gums and Resins, Chapter 22, 1980). The ionic derivatives have the advantage that they are soluble in cold water and thus cover a large range of applications. Carboxymethyl derivatives (for example, carboxymethyl starch or carboxymethyl cellulose) and oxidized polysaccharides are the best known representatives of ionic derivatives. These derivatives have only one ionic group (carboxyl group) per substituent and are not suitable in an advantageous manner, for example, as co-builders in detergents or water softening agents. In addition, esters of adipic acid (adipate), succinic acid (succinate) or maleic acid are common which result from esterification of the dicarboxylic acid with the glucose of the starch or cellulose. However, in this

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MARKED-UP VERSION OF PAGE 2

reaction one of the functional groups of the two carboxylic groups is lost. This is of great disadvantage when this derivative is to be used as a complexing agent for polyvalent ions (for example, calcium). For example, this complexing property would be advantageous in regard to water softening agents.

A derivative produced from maleic acid anhydride and starch (or cellulose) in a Michael addition in alkaline medium would not lose this advantage. In this reaction, a hydroxy group of the glucose reacts with a double bond of the maleic acid with formation of an ether and with conservation of the two functional carboxyl groups. In this reaction a succinic acid ether of the starch is formed (a succinyl starch, not starch succinate, the latter would be a succinic acid ester). The disadvantage in this connection is that the yields of the maleic acid are minimal (conventionally less than 10 %) and the achievable substitution rate is small. Accordingly, it is not economical and not sufficiently efficient in its effects. Additions to a double bond with glucose or other carbohydrates are generally not efficient. Moreover, the maleic acid anhydride reacts with the starch to maleic acid ester (starch maleate) in this Michael reaction under alkaline conditions, so that in this reaction also one of the two carboxyl groups is lost as an ionic group (see R. L. Davidson, "Handbook of Water-soluble Gums and Resins", Chapter 22, pp. 22-40, 1980).

Summary of the Invention

In particular in connection with the natural base of polysaccharides there is still a high need in regard to polysaccharide derivatives with multi-functional properties. The object of the invention resides therefore in the provision of polysaccharide derivatives in which both carboxyl groups are preserved.

Surprisingly, new malatyl polysaccharides were found which can be prepared from polysaccharides and cis-epoxy succinate or other epoxy carboxylic acids, wherein the carboxyl groups are maintained in their preparation. However, it is also possible to use the derivatives of polysaccharides instead of native polysaccharides. This

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hygiene articles or in the medical field. For a very great degree of crosslinking, they can swell only minimally and can be used, for example, as ion exchangers for aqueous system or as additives in pharmaceutical applications (for example, tablet bursting agents, suspension stabilizers etc.).

Description of Preferred Embodiments

In the following, embodiments of the invention will be explained in more detail.

Example 1

Malatyl Starch from Potato Starch and Disodium Epoxy Succinate made from Maleic Acid

Step 1A

Maleic acid reacts very quickly and completely with H_2O_2 and 2 mol-% of a catalyst in only 1.5 hours at 65 °C to disodium epoxy succinate in almost quantitative yield: maleic acid + H_2O_2 + NaOH + sodium tungstate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$).

Into a one-liter round flask with stirrer, thermometer, and dropping funnel, a solution of 116 g (1.0 mole) maleic acid in 300 ml water is introduced. To this solution a solution of 60 g (1.5 mole) NaOH in 100 ml water is added. As a result of the released neutralization heat, the temperature rises to approximately 70 °C. To the hot solution 6.6 g (0.02 mole) of sodium tungstate are added.

A pH electrode is immersed into the solution and 1.2 mole of a 30-% H_2O_2 (123 ml or 136 g; for 35-% H_2O_2 it is 103 ml or 117 g) are added. The exothermic reaction is maintained for 15 minutes with a water bath at 65 °C, and the pH value drops from approximately 5.5 to 4. With dropwise addition of a solution of 0.5 mole (20 g) NaOH in 100 ml water the reaction solution is then maintained at a minimum of pH 4. After 1-1.5 hours of stirring at approximately 65 °C, the solution is cooled to

MARKED-UP VERSION OF PAGE 1

Malatyl Polysaccharides, Their Production and Their Use

Background of the Invention

1. Field of the Invention

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Reactions of starch or cellulose to ionic derivatives have also been described often (see, inter alia, R. L. Davidson, Handbook of Water-soluble Gums and Resins, Chapter 22, 1980). The ionic derivatives have the advantage that they are soluble in cold water and thus cover a large range of applications. Carboxymethyl derivatives (for example, carboxymethyl starch or carboxymethyl cellulose) and oxidized polysaccharides are the best known representatives of ionic derivatives. These derivatives have only one ionic group (carboxyl group) per substituent and are not suitable in an advantageous manner, for example, as co-builders in detergents or water softening agents. In addition, esters of adipic acid (adipate), succinic acid (succinate) or maleic acid are common which result from esterification of the dicarboxylic acid with the glucose of the starch or cellulose. However, in this

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A pH electrode is immersed into the solution and 1.2 mole of a 30-% H_2O_2 (123 ml or 136 g; for 35-% H_2O_2 it is 103 ml or 117 g) are added. The exothermic reaction is maintained for 15 minutes with a water bath at 65 °C, and the pH value drops from approximately 5.5 to 4. With dropwise addition of a solution of 0.5 mole (20 g) NaOH in 100 ml water the reaction solution is then maintained at a minimum of pH 4. After 1-1.5 hours of stirring at approximately 65 °C, the solution is cooled to

Abstract of the Disclosure

Malatyl polysaccharides can be prepared from polysaccharides and cis-epoxy succinate or other epoxy carboxylic acids, wherein the carboxyl groups are maintained in this reaction. It is also possible to use derivatives of polysaccharides instead of native polysaccharides. The reaction makes possible the preparation of products with multi-variable properties. The malatyl polysaccharides can be used as thickening agents, complexing agents for cations or organic compounds, as ion exchangers for aqueous systems, as adjuvants in pharmaceutical applications, and as ingredients for hygiene articles.

Malatyl Polysaccharides, Their Production and Their Use

The invention relates to malatyl polysaccharides made of polysaccharides and cis-epoxy succinate or other epoxy carboxylic acids, methods for their production as well as their use in detergents, thickening agents, complexing agents for cations or organic compounds or as ion exchangers for aqueous system or as adjuvants in pharmaceutical applications (for example, tablet bursting agents, suspension stabilizes etc.) or as ingredients in hygiene articles and medical fields.

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Reactions of starch or cellulose to ionic derivatives have also been described often (see, inter alia, R. L. Davidson, Handbook of Water-soluble Gums and Resins, Chapter 22, 1980). The ionic derivatives have the advantage that they are soluble in cold water and thus cover a large range of applications. Carboxymethyl derivatives (for example, carboxymethyl starch or carboxymethyl cellulose) and oxidized polysaccharides are the best known representatives of ionic derivatives. These derivatives have only one ionic group (carboxyl group) per substituent and are not suitable in an advantageous manner, for example, as co-builders in detergents or water softening agents. In addition, esters of adipic acid (adipate), succinic acid (succinate) or maleic acid are common which result from esterification of the dicarboxylic acid with the glucose of the starch or cellulose. However, in this

reaction one of the functional groups of the two carboxylic groups is lost. This is of great disadvantage when this derivative is to be used as a complexing agent for polyvalent ions (for example, calcium). For example, this complexing property would be advantageous in regard to water softening agents.

5 A derivative produced from maleic acid anhydride and starch (or cellulose) in a Michael addition in alkaline medium would not lose this advantage. In this reaction, a hydroxy group of the glucose reacts with a double bond of the maleic acid with formation of an ether and with conservation of the two functional carboxyl groups. In this reaction a succinic acid ether of the starch is formed (a succinyl starch, not starch succinate, the latter would be a succinic acid ester). The disadvantage in this connection is that the yields of the maleic acid are minimal (conventionally less than 10 %) and the achievable substitution rate is small. Accordingly, it is not economical and not sufficiently efficient in its effects. Additions to a double bond with glucose or other carbohydrates are generally not efficient. Moreover, the maleic acid anhydride reacts with the starch to maleic acid ester (starch maleate) in this Michael reaction under alkaline conditions, so that in this reaction also one of the two carboxyl groups is lost as an ionic group (see R. L. Davidson, "Handbook of Water-soluble Gums and Resins", Chapter 22, pp. 22-40, 1980).

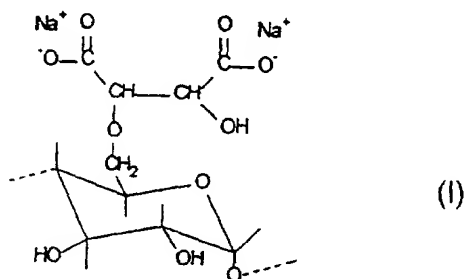
10 In particular in connection with the natural base of polysaccharides there is still a high need in regard to polysaccharide derivatives with multi-functional properties. The object of the invention resides therefore in the provision of polysaccharide derivatives in which both carboxyl groups are preserved.

15 Surprisingly, new malatyl polysaccharides were found which can be prepared from polysaccharides and cis-epoxy succinate or other epoxy carboxylic acids, wherein the carboxyl groups are maintained in their preparation. However, it is also possible to use the derivatives of polysaccharides instead of native polysaccharides. This

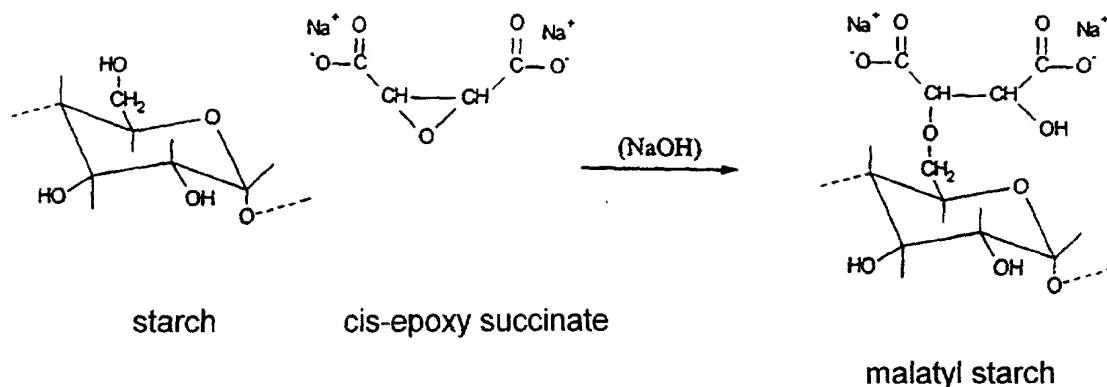
makes possible the preparation of products with multi-variable properties.

5 The preparation of malatyl polysaccharides can be realized with solid epoxy succinate as well as with a epoxy succinate solution. This has the advantage that it is not required to start with pure epoxy succinate but instead one can produce it in situ from other inexpensive starting materials (by a known method). For example, it is possible to produce the cis-epoxy succinate from maleic acid and hydrogen peroxide or from hydroquinone and hydrogen peroxide. The solution can be concentrated in vacuum, and the concentrated epoxy succinate solution is then added as a reagent to the starch, which is made alkaline, in an alcohol suspension or acetone suspension.

An advantageous compound according to the invention is malatyl starch, a malic acid ether of starch of the general formula (I):



15 The malatyl starch is obtained by the reaction of cis-epoxy succinate (disodium salt of cis-epoxy succinic acid) with starch in an alkaline suspension. The use of epoxy succinic acid itself is also possible, but in this case an equivalent amount of base must be added previously in the basification step. Schematic:



Producing epoxy succinate itself (and other epoxy carboxylic acids) is described in several publications (DE 2213260; DE 2347224; G.B. Payne, P.H. Williams, J. Org. Chem., 24, pp. 54ff, 1959; G.B. Payne, J. Org. Chem., 24, p. 2048ff, 1959; E. Weitz, H. Schobbert, H. Seibert, Chem. Ber., 68, p. 1163, 1935).

The reaction of cis-epoxy succinate or other epoxy carboxylic acids with starch, cellulose, or other polysaccharides is however unknown. Currently, no indication has been found that these substances (for example, malatyl starch) have been described in any other publication.

Also, it has been attempted to produce ionic starch derivatives or polysaccharides derivatives with other epoxy carboxylic acids. These include, inter alia, epoxy crotonic acid, epoxy cinnamic acid, epoxy acrylic acid or epoxy aconitic acid. However, for these epoxy carboxylic acids only average to low yields were obtained so that only low substitution rates will be adjustable.

In addition to the preparation of malatyl starch from starch with an epoxy succinate solution, the preparation of malatyl starch from solid epoxy succinate and basified

starch is the more elegant method because there is no possibility of introducing contaminants of the epoxy succinate preparation. However, a possible introduction of contaminants is not of great importance because the malatyl starch at the end of the preparation process is filtered from the suspension and is washed with an alcohol and water mixture.

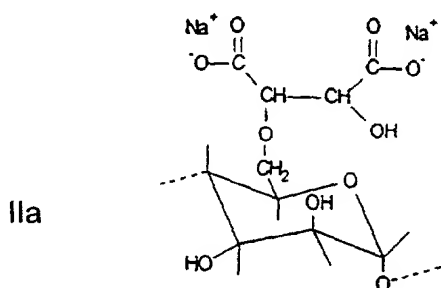
For obtaining improved substitution yields, it was found to be beneficial to adjust a pH value of 9-13 with sodium hydroxide in the alcohol suspension and to employ a molar ratio of NaOH to starch that is not higher than 1:1 to 2:1 but to work as much as possible with smaller ratios. Advantageous is a NaOH concentration of approximately 3-5 mol/l. The ratio depends also on which molar amount of cis-epoxy succinate is used. When a greater molar ratio of epoxy succinate/starch is selected, more NaOH must be employed for a better activation of the starch (in this connection, the limit NaOH/starch of 1/1 to 2/1 should also be observed). The yields of epoxy succinate are approximately 40-85 % so that a substitution rate of 0.2 to 0.6 is easily adjustable.

The fully neutralized malatyl starch (as a sodium salt) with a substitution ratio of 0.15 to 0.6 can be easily dissolved in cold water, the solutions are clear, and have a pH value of 7.8-8.1. The unneutralized acid form of the malatyl starch is sparingly soluble in water and has a pH value of 2.5-2.8 as a suspension of 1 %.

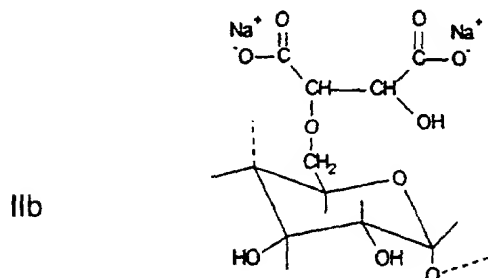
After the reaction the malatyl starch can be adjusted with hydrochloric acid, acetic acid or other acids to the desired pH value. This is performed advantageously in an alcohol suspension wherein the contents of water of the suspension medium should be a minimum of 15 % and a maximum of 30 %. The adjustment of the pH value has a great influence on the final properties of the malatyl starch. When drying the partially neutralized malatyl starch compounds, having a pH value of 3.0-7.5, an intermolecular and intramolecular cross-linking occurs which results in that

the malatyl starch becomes insoluble in water and forms viscous to highly viscous gels. When using at the same time a di-functional or poly-functional cross-linking agent (for example, an organic dichloro compound during the reaction), it is also possible to obtain stable gel-forming products.

- 5 A further advantageous compound according to the invention is the group of malatyl galactomannans of the general formula (IIa) on the basis of mannose



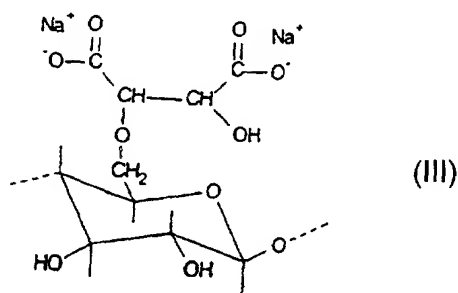
and/or the general formula (IIb) based on galactose.



- 10 In analogy to the preparation of malatyl starch, the malatyl guaran can also be produced from cis-epoxy succinate and guaran. The preparation of malatyl guaran is also carried out in suspension. It is advantageous to use methanol and isopropanol with approximately 20 % water. The basification should be carried out with sodium hydroxide at approximately 20 °C. The yields relative to cis-epoxy succinate are somewhat less than for the malatyl starch preparation. The solutions
- 15

of malatyl guaran are more viscous than those of malatyl starch.

A further advantageous compound according to the invention is malatyl cellulose of the general formula (III)



Malatyl cellulose can be produced from cellulose and cis-epoxy succinate. Advantageously, the reaction is carried out in isopropanol with a total of approximately 20 % water and a previous basification with sodium hydroxide at approximately 15 °C. Heating during basification does not provide any advantages. The yields relative to cis-epoxy succinate are worse than for the malatyl starch preparation. The solutions of malatyl cellulose are more viscous than those of malatyl starch.

The final properties of malatyl cellulose and malatyl guaran can also be varied by adjusting the pH value before drying so that in this connection also cross linking can be adjusted.

The compounds according to the invention are suitable as a result of their properties in their un-crosslinked form, as complexing agents for polyvalent cations, for example, in detergents or for organic substances in the pharmaceutical sector. In their crosslinked form they are suitable as thickening agents because they are insoluble in water, swell strongly and form gels. Depending on the density of the crosslinking, slightly or highly viscous gels form which can be used, for example, in

hygiene articles or in the medical field. For a very great degree of crosslinking, they can swell only minimally and can be used, for example, as ion exchangers for aqueous system or as additives in pharmaceutical applications (for example, tablet bursting agents, suspension stabilizers etc.).

5 In the following, embodiments of the invention will be explained in more detail.

Example 1

Malatyl Starch from Potato Starch and Disodium Epoxy Succinate made from Maleic Acid

Step 1A

10 Maleic acid reacts very quickly and completely with H_2O_2 and 2 mol-% of a catalyst in only 1.5 hours at 65 °C to disodium epoxy succinate in almost quantitative yield: maleic acid + H_2O_2 + NaOH + sodium tungstate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$).

15 Into a one-liter round flask with stirrer, thermometer, and dropping funnel, a solution of 116 g (1.0 mole) maleic acid in 300 ml water is introduced. To this solution a solution of 60 g (1.5 mole) NaOH in 100 ml water is added. As a result of the released neutralization heat, the temperature rises to approximately 70 °C. To the hot solution 6.6 g (0.02 mole) of sodium tungstate are added.

20 A pH electrode is immersed into the solution and 1.2 mole of a 30-% H_2O_2 (123 ml or 136 g; for 35-% H_2O_2 it is 103 ml or 117 g) are added. The exothermic reaction is maintained for 15 minutes with a water bath at 65 °C, and the pH value drops from approximately 5.5 to 4. With dropwise addition of a solution of 0.5 mole (20 g) NaOH in 100 ml water the reaction solution is then maintained at a minimum of pH 4. After 1-1.5 hours of stirring at approximately 65 °C, the solution is cooled to

40 °C, and the rest of the last NaOH solution is added.

The solution is concentrated at 30-40 °C in vacuum to approximately 300 ml.

Step 1B

190 g (1.0 mole) potato starch (moisture contents 15 %) are suspended in 500 ml ethanol in a four-neck glass flask provided with a stirrer, thermometer, and dropping funnel. 80 g of a 50 % by weight sodium hydroxide solution is added to the suspension under stirring within 5 minutes. The mixture is stirred for 30 minutes at a temperature of 20-25 °C. Subsequently, 150 ml of the concentrated epoxy succinate solution of step 1A is added to the flask at 25 °C. The reaction mixture is then heated within 30 minutes to 70 °C and is stirred for 4 hours at this temperature. After cooling to 20-25 °C, the suspension is filtered and the residue is washed twice with 80 % methanol and with pure methanol. The malatyl starch is then dried at 110 °C in a circulating air drying chamber to a residual moisture of approximately 5-10 %. A substitution rate DS = 0.35 is achieved (titration of the acidic form). In the following, this malatyl starch is identified with MS/W or MS35/W.

Example 2

Malatyl Starch from Potato Starch and Disodium Epoxy Succinate
made from Hydroquinone

Step 2A

Disodium epoxy succinate from: hydroquinone + H_2O_2 + NaOH

The oxidation of hydroquinone by alkali and H_2O_2 takes place - via the quinone - as

that of the quinone itself. For preparative purposes, it is therefore simpler to employ hydroquinone. The reaction takes place with great heat development and is finally very vigorous. However, with a suitable selection of the reaction conditions and flasks cooling is not required.

5 In a 5-l beaker with magnetic stirrer, 110 g (1 mole) hydroquinone together with 690 ml 35-% (8 mole) H_2O_2 is heated under stirring to 70-80 °C (there is hardly any gas development to be observed) and then a NaOH solution (of 120 g NaOH and 500 ml water) is added so fast or so slow via a dropping funnel that the vigorous reaction will not become too violent. The mixture turns a dark reddish brown upon adding the NaOH and additional heat is developed. Approximately 5 minutes after completed NaOH addition, the reaction is completed, and the solution is colorless. The solution is then concentrated at 30-40 °C in vacuum to 200-300 ml.

Step 2B

15 190 g (1.0 mole) potato starch (moisture contents 15 %) are suspended in 500 ml ethanol in a four-neck glass flask provided with a stirrer, thermometer, and dropping funnel. 80 g of a 50 % by weight sodium hydroxide solution is added to the suspension under stirring within 5 minutes. The mixture is stirred for 30 minutes at a temperature of 20-25 °C. Subsequently, 150 ml of the concentrated epoxy succinate solution of step 2A is added to the flask at 25 °C. The reaction mixture is then heated within 30 minutes to 70 °C and is stirred for 4 hours at this temperature. After cooling to 20-25 °C, the suspension is filtered and the residue is washed twice with 80 % methanol and with pure methanol. The malatyl starch is then dried at 110 °C in a circulating air drying chamber to a residual moisture of approximately 5-10 %. A substitution rate $DS = 0.15$ is achieved (titration of the acidic form). In the following, this malatyl starch is identified with MS/H or MS15/W.

Example 3

Malatyl Starch from Potato Starch and Disodium Epoxy Succinate

Step 3A

Preparation of disodium epoxy succinate, as described in step 1A. Isolation:

- 5 The solution is concentrated at 30-40 °C in vacuum to 300 ml and is introduced with stirring into 1.5 liter acetone to thereby precipitate 160 g of colorless disodium epoxy succinate. The precipitated product is filtered and washed with acetone.

Step 3B

10 190 g (1.0 mole) potato starch (moisture contents 15 %) are suspended in 400 ml ethanol in a four-neck glass flask provided with a stirrer, thermometer, and dropping funnel. 80 g of a 50 % by weight sodium hydroxide solution is added to the suspension under stirring within 5 minutes. The mixture is stirred for 30 minutes at a temperature of 20-25 °C. Subsequently, 150 g (0.85 mole) solid disodium epoxy succinate of step 3A is added in portions to the flask at 25 °C. The reaction mixture is then heated within 30 minutes to 50 °C and is stirred for 4 hours at this temperature. After cooling the suspension to 20 °C, it is neutralized with acetic acid (99 %) to a pH of 8-9, then filtered and the residue is washed twice with 80 % methanol and with pure methanol. The malatyl starch is then dried at 110 °C in a circulating air drying chamber to a residual moisture of approximately 5-10 %. A substitution ratio DS = 0.5 is achieved (titration of the acid form). In the following, this malatyl starch is identified with MS05.

Example 4

Malatyl Guaran from Guar Flour and Disodium Epoxy Succinate

42 g (0.26 mole) guar flour (moisture contents 9 %) are suspended in 400 ml isopropanol and 60 ml water in a four-neck glass flask provided with stirrer, thermometer and dropping funnel. 20 g of a 50 % by weight NaOH solution is added under stirring to the suspension. The mixture is then stirred for 30 minutes at a temperature of 20 °C. Subsequently, 31 g (0.176 mole) solid disodium epoxy succinate of step 3A is added to the flask in portions at 25 °C. The reaction mixture is then heated within 30 minutes to 60 °C, is stirred for 4 hours at this temperature, and allowed to stand over night. The cooled suspension is neutralized with acetic acid (99 %) to a pH of 8-9, then filtered and the residue is washed twice with 80 % methanol and with pure methanol. The malatyl guaran is then dried at 110 °C in a circulating air drying chamber to a residual moisture of approximately 5-10 %. A substitution ratio DS = 0.4 is achieved (titration of the acid form).

Example 5

Malatyl Cellulose from Fir Cellulose Powder and Disodium Epoxy Succinate

41 g (0.25 mold) cellulose (moisture contents 4 %) are suspended in 400 ml isopropanol and 80 ml water in a four-neck glass flask provided with stirrer, thermometer and dropping funnel. 10 g NaOH (scales) are added under stirring to the suspension. The mixture is stirred for 60 minutes at a temperature of approximately 15 °C. Subsequently, 53 g (0.3 mole) solid disodium epoxy succinate (see step 3A) is added to the flask in portions at 25 °C. The reaction mixture is then heated within 30 minutes to 70 °C and stirred for 4 hours at this temperature. After cooling the suspension to 20-25 °C, it is neutralized with acetic acid (99 %) to a pH of 8-9, then filtered and the residue is washed twice with 80 % methanol and with pure methanol. The malatyl cellulose is then dried at 110 °C in a circulating air drying chamber to a residual moisture of approximately 5-10 %. A substitution ratio DS = 0.6 is achieved (titration of the acid form).

The structural examinations by means of infrared spectroscopy (FT-IR) and nuclear magnetic resonance spectroscopy (^{13}C -NMR) show that these are starch derivatives which contain unequivocally carboxyl groups (see in this connection Figs. 1 through 4 for FT-IR and Figs. 5 and 6 for ^{13}C -NMR as well as comparative Tables 1 and 2).

The typical starch bands show at 1021 to 1236 cm^{-1} and the bands for the carboxyl group can be seen clearly at 1609 and 1607 cm^{-1} (-COO) and at 1703 and 1706 (-COOH). No ester bands at 1760 cm^{-1} are present. The resonance peaks of carbon of the carboxyl group can be identified at 178.2 and 176.5 ppm. Resonance peaks of the ester at approximately 160 ppm are also not present here so that the presence of an ether can be assumed.

Examinations by means of gel permeation chromatography (GPC) show unequivocally that the desired high molecular substances are present (see in this connection Figs. 7 and 8 for MS15/H and Figs. 9 and 10 for MS35/W). The molecular weights are approximately 2 to 8 million g/mole. A 1 % solution has an average viscosity of 500-1000 mPa.s (depending on the substitution rate).

Table 1: Comparison of the Bands (cm^{-1}) of the FT-IR Spectra (Figs. 1 and 2)

MS35/W	MS15/H	potato starch
530	529	525
576	577	580
--	--	615
708	709	710
762	763	762
848	850	855
931	931	931

1021	1022	1022
1082	1082	1081
1156	1156	1158
1236	1236	1236
1391	1370	1364
1607	1609	--
--	--	1650
1706	1703	--

Table 2: Comparison of Resonance Peaks (ppm) of ^{13}C -NMR Spectra (Figs. 5 and 6)

MS15/H	MS35/H
61.2	61.2
70.1	
71.8	71.8
72.1	72.1
73.8	73.8
77.8	77.8
80.0	
81.6	
82.5	83.8
100.1	100.1
176.5	178.2

The malatyl derivatives are stable and can be stored without problems so that no

structural or property changes will result (average storage at 25±3 °C and 60±5 % humidity).

Example 6 Use as Complexing Agent

5 The assay was carried out according to the calcium carbonate method. For this purpose, 1 g of malatyl starch was dissolved in 100 ml distilled water, 10 ml of a 2 % sodium carbonate solution was added, and then calcium acetate mono hydrate solution (with 44.1 g/l) was used for titration up to permanent turbidity.

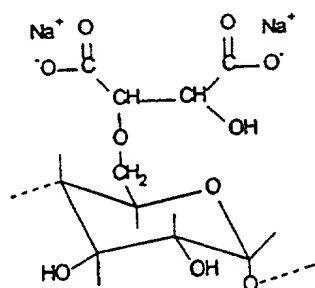
Table 3: Complexing Results

substance	DS	mg/g
malatyl starch MS/H	0.15	110
malatyl starch MS/W	0.35	225
malatyl starch MS05	0.5	320
succinic acid, disodium (comparison)		250
penta-sodium triphosphate (comparison)		200

10 According to this method, the complexing behavior of the substance malatyl starch according to the invention is better than that of pure succinic acid and that of pentasodium triphosphate, relative to the employed amount (in mg/g). Moreover, it was found that the formed turbidity (CaCO_3) did not precipitate immediately but
15 sedimentation of the turbidity took several hours when using malatyl starch and occurred only after days when using MS/H.
20

Claims:

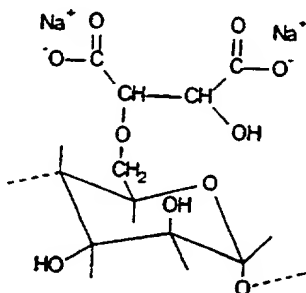
1. Malatyl polysaccharides obtainable by reaction of polysaccharides and cis-epoxy succinate or epoxy carboxylic acids.
2. Compound according to claim 1, in particular malatyl starch of the general formula (I)



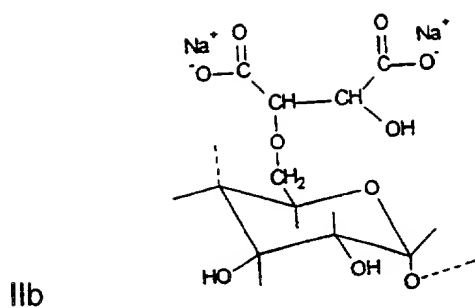
(I)

3. Compound according to claim 1, in particular malatyl galactomannan of the general formula

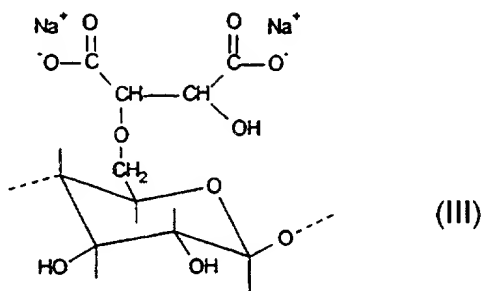
Ila



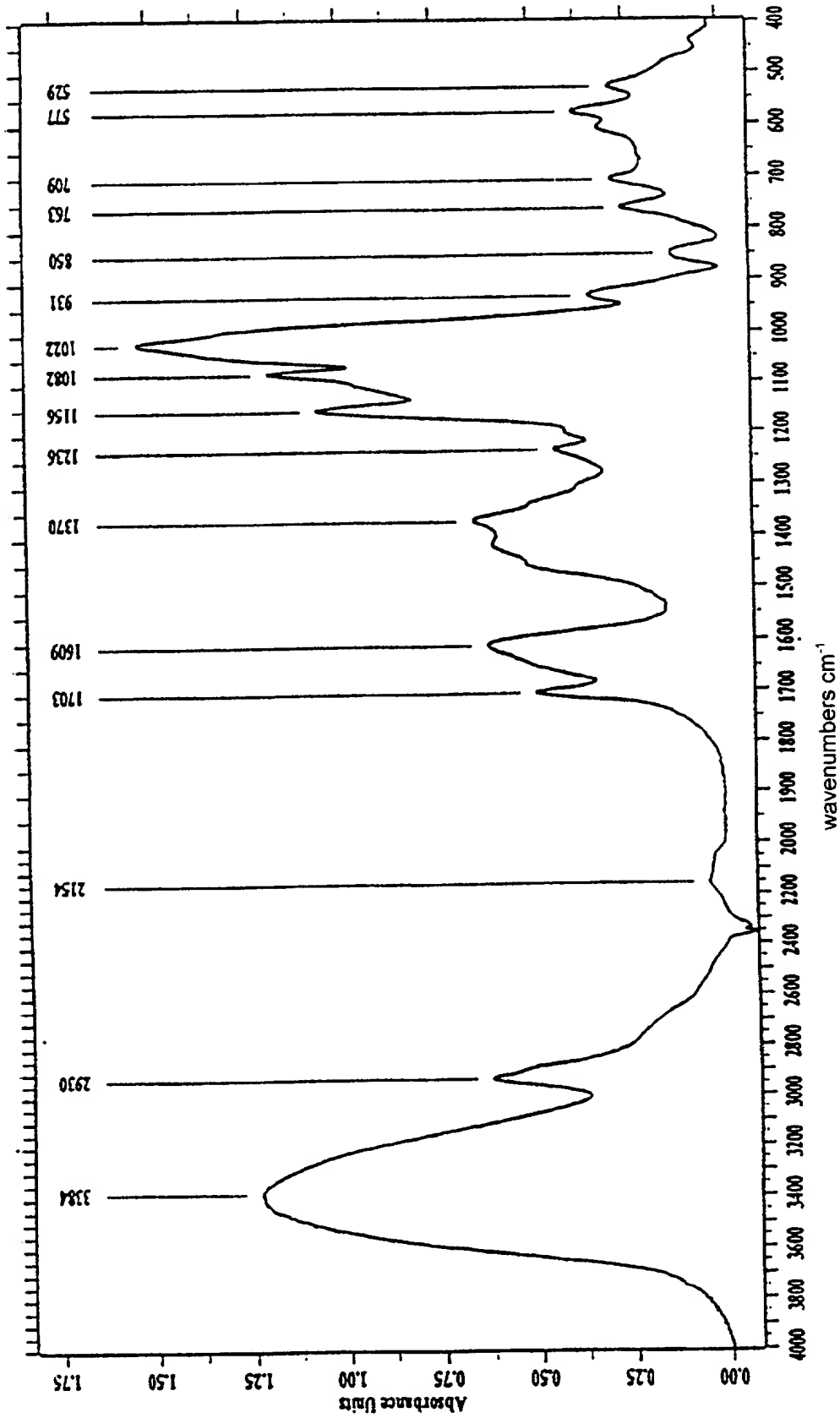
and/or



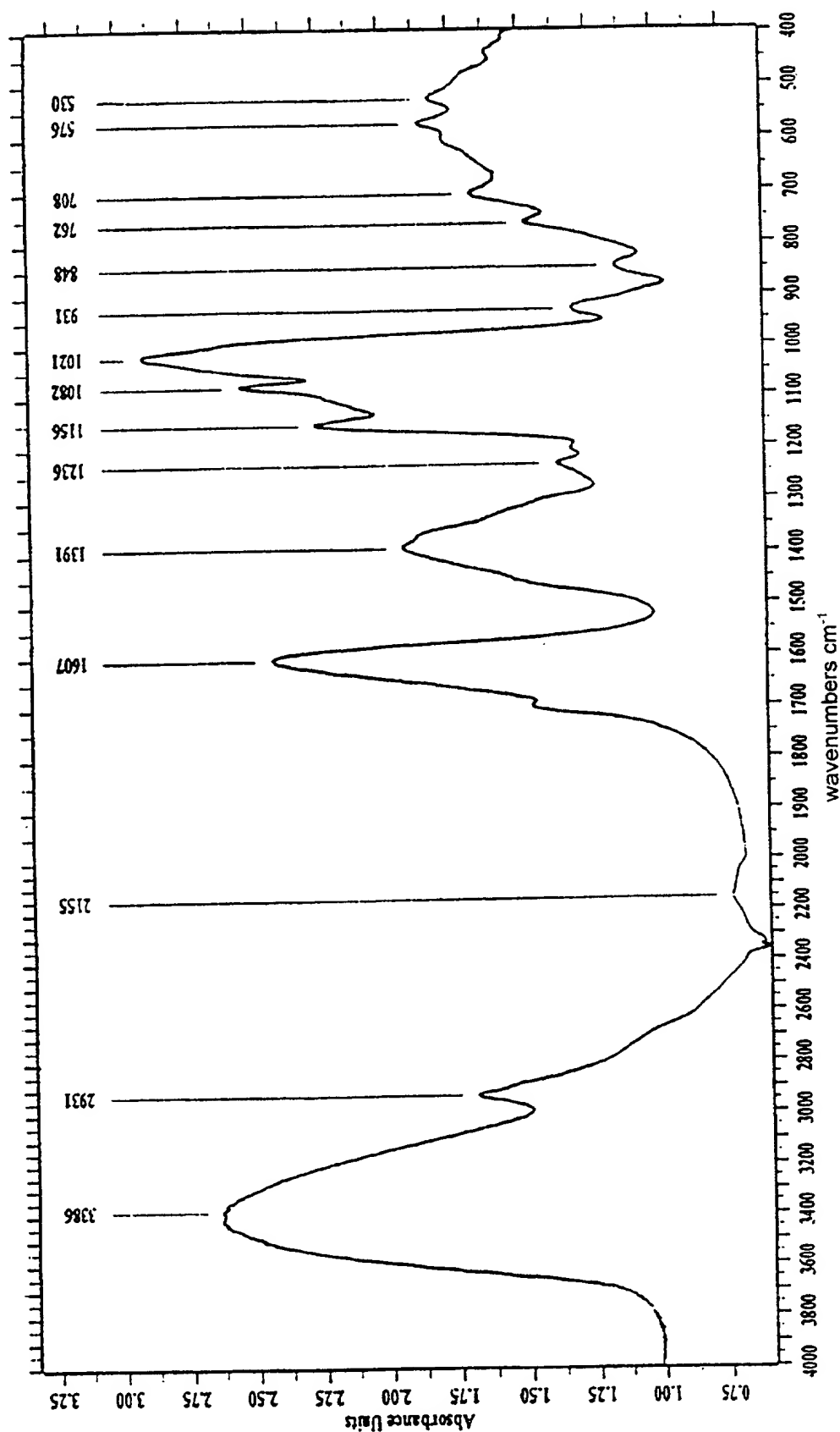
4. Compound according to claim 1, in particular malatyl cellulose of the general formula (III).



5. Method for preparing compounds according to claim 1, characterized in that polysaccharides are reacted with cis-epoxy succinate or analog epoxy carboxylic acids.
6. Method according to claim 5, characterized in that the reaction and the conversion of polysaccharides with epoxy succinate are carried out in suspension or in a solid phase reaction.
7. Use of compounds according to one of the claims 1 to 4 as thickening agent or as complexing agents for cations or organic compounds or as ion exchangers for aqueous systems or as adjuvants in pharmaceutical applications (for example, tablet bursting agents, suspension stabilizers etc.) or as ingredients for hygiene articles.

**Fig. 1**

Sample: malatyl starch/Hy	Frequency range: 3999.6401-399.1926	Number of Scans: 50
Method: KBr	Resolution: 4.0	Scan duration: 48.0520 (sec)
	Support points: 2	Acquisition: double-sided, forward-backward

**Fig. 2**

Sample: malatyl starch/W	Frequency range: 3999.6401-399.1926	Number of Scans: 50
Method: KBr	Resolution: 4.0	Scan duration: 48.0463 (sec)
File5MS_W_DIA.0	Support points: 2	Acquisition: double-sided, forward-backward

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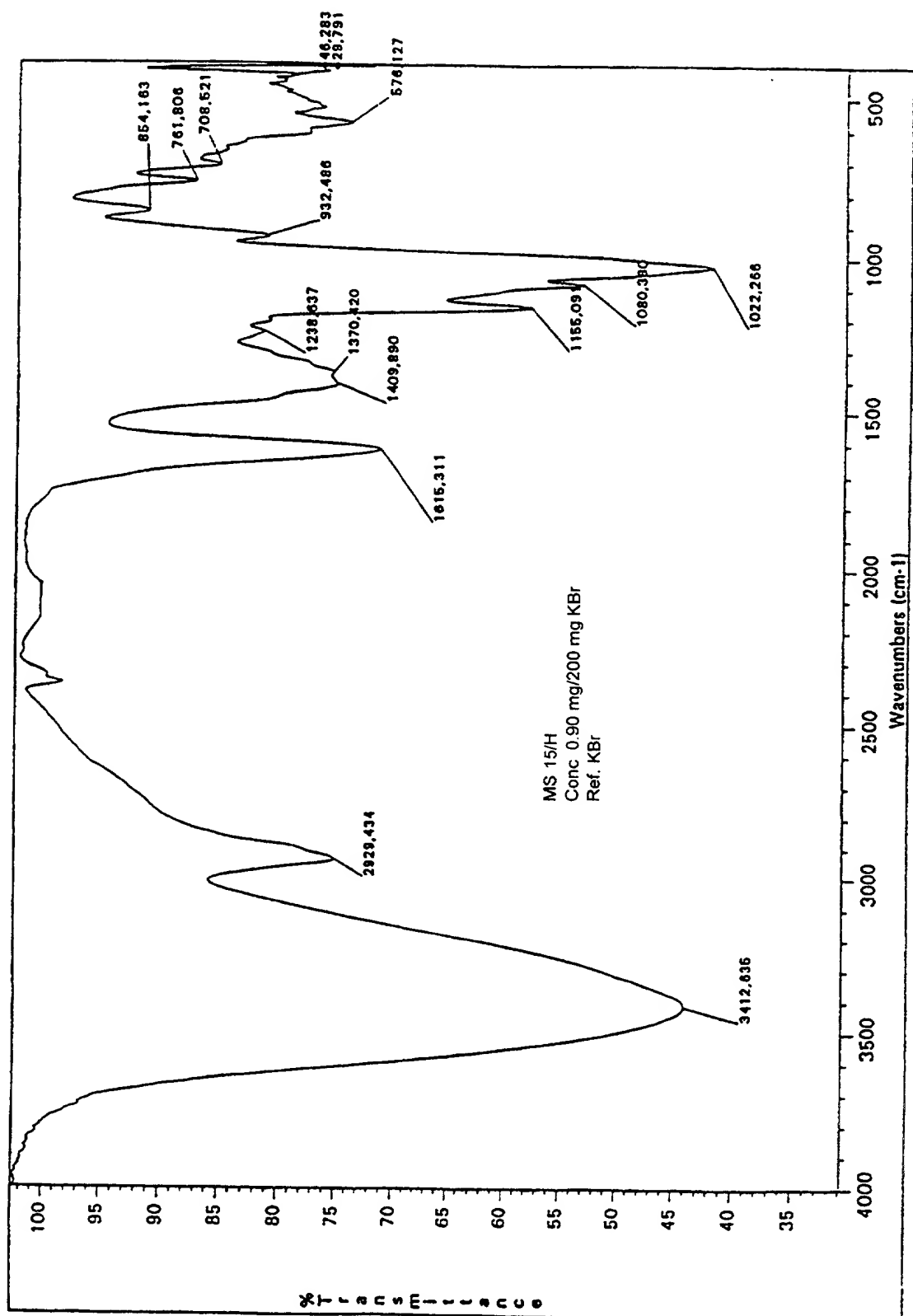


Fig. 3

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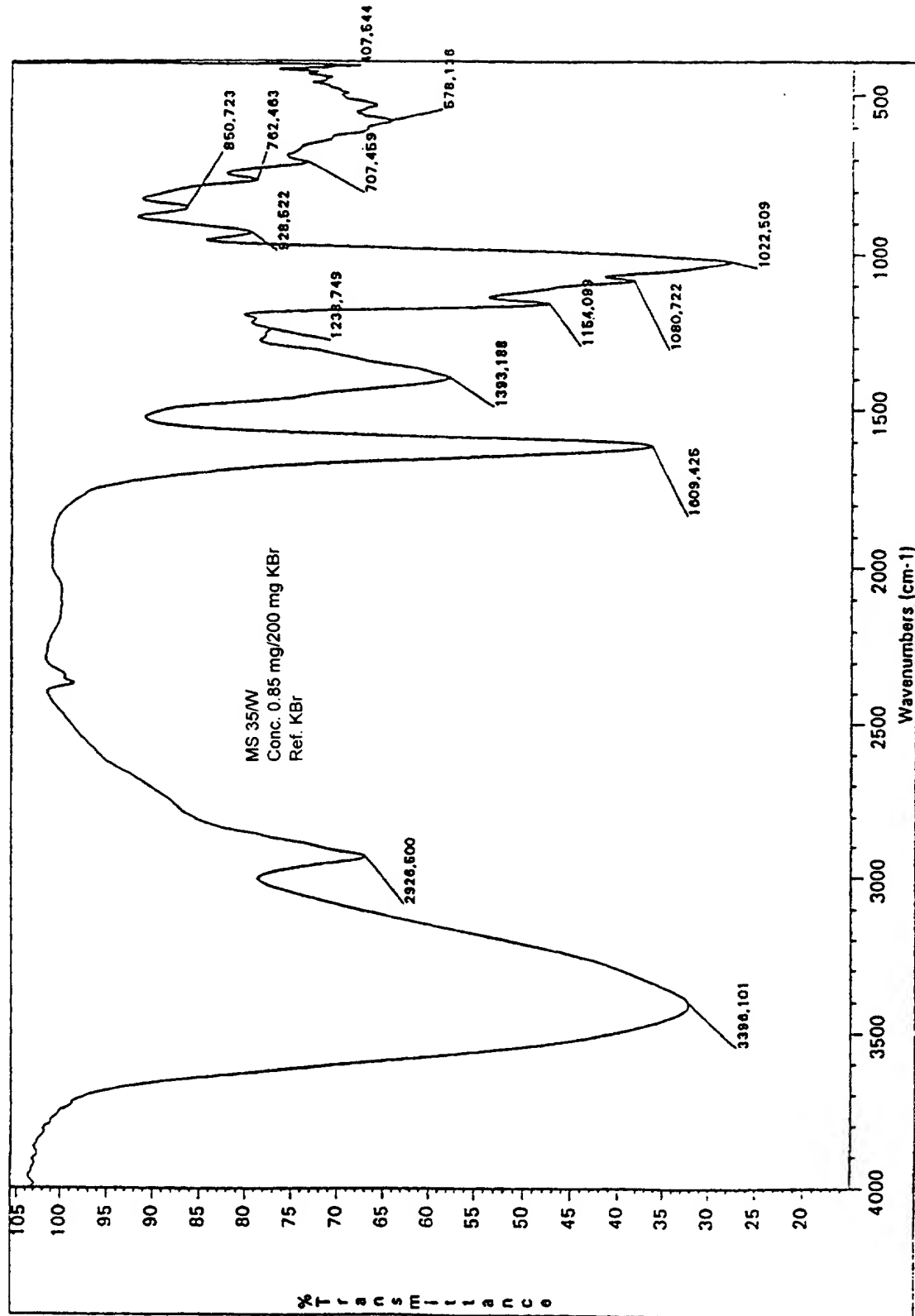


Fig.4

05/10

Current Data Parameters

EXPNO 152
PROCNO 1

F2 - Acquisition Parameters

Time 9.14
INSTRUM spect
PROBHD 5 mm HX111nu
PULPROG zgpg30
TD 65536
SOLVENT D2O
NS 10000
DS 4
SWH 26581.721 Hz
FIDRES 3.261460 Hz
AQ 0.1524212 sec
RG 7290.2
DM 16.000 usec
DE 4.50 usec
TE 300.2 K
D12 0.00000500 sec
PL13 18.00 dB
D1 0.85000002 sec
CPROG2 waltz16
P31 100.00 usec
SF02 400.1320000 MHz
NUC2 1H
PL2 -3.00 dB
PL12 18.00 dB
P1 8.60 usec
DE 4.50 usec
SF01 100.6243412 MHz
NUC1 13C
PL1 0.00 dB
D11 0.03000000 sec

F2 - Processing parameters

SF 32768
SF 100.6127716 MHz
EN
WDW 0
SSB 0
LB 10.00 Hz
GB 0
PC 1.10

1D NMR plot parameters

CX 20.00 cm
FIP 188.999 gpa
F1 19015.76 Hz
F2 46.326 ppa
F2 4660.92 Hz
PPHCK 7.13171 gpa/°
H/Lm 717.4290 Hz/Lm

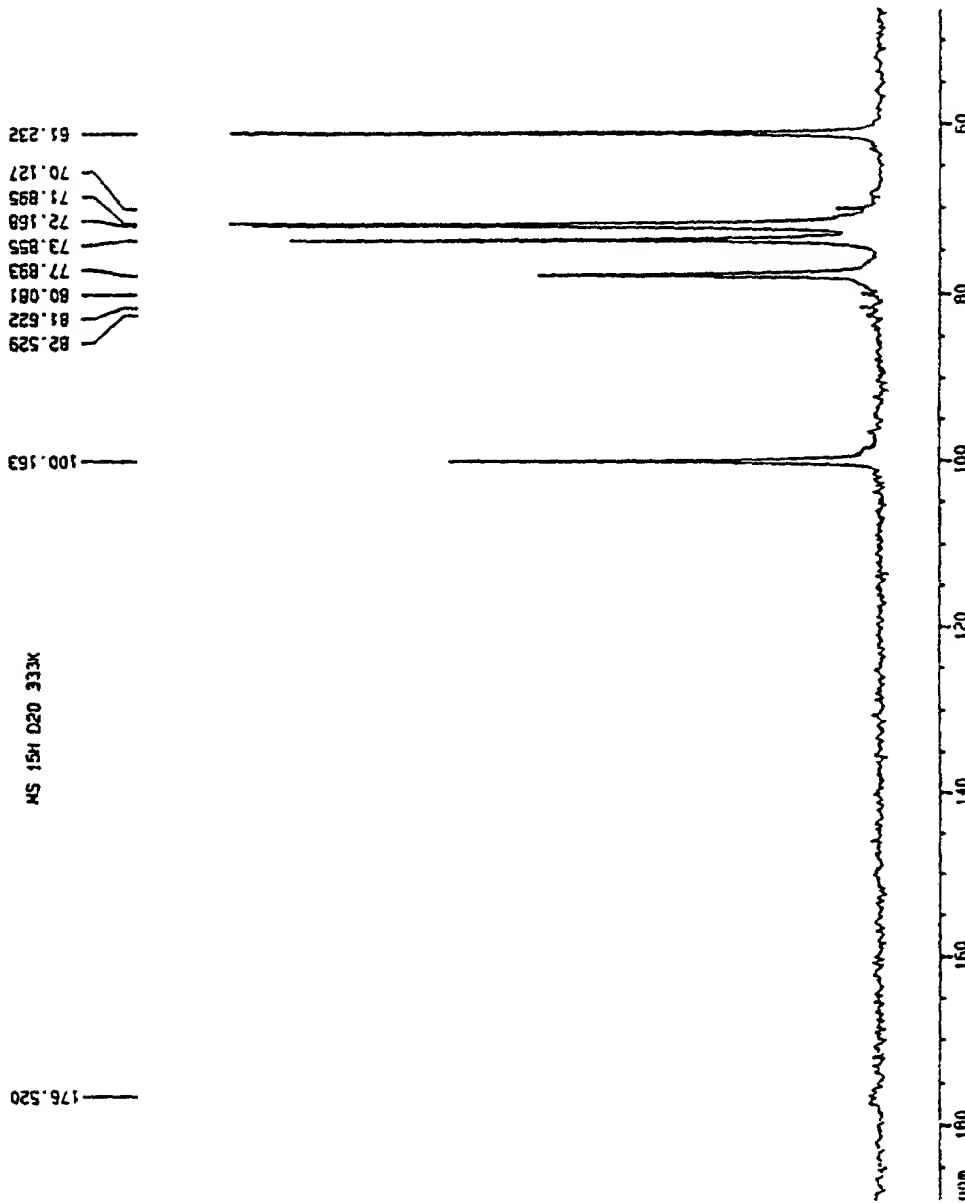


Fig. 5

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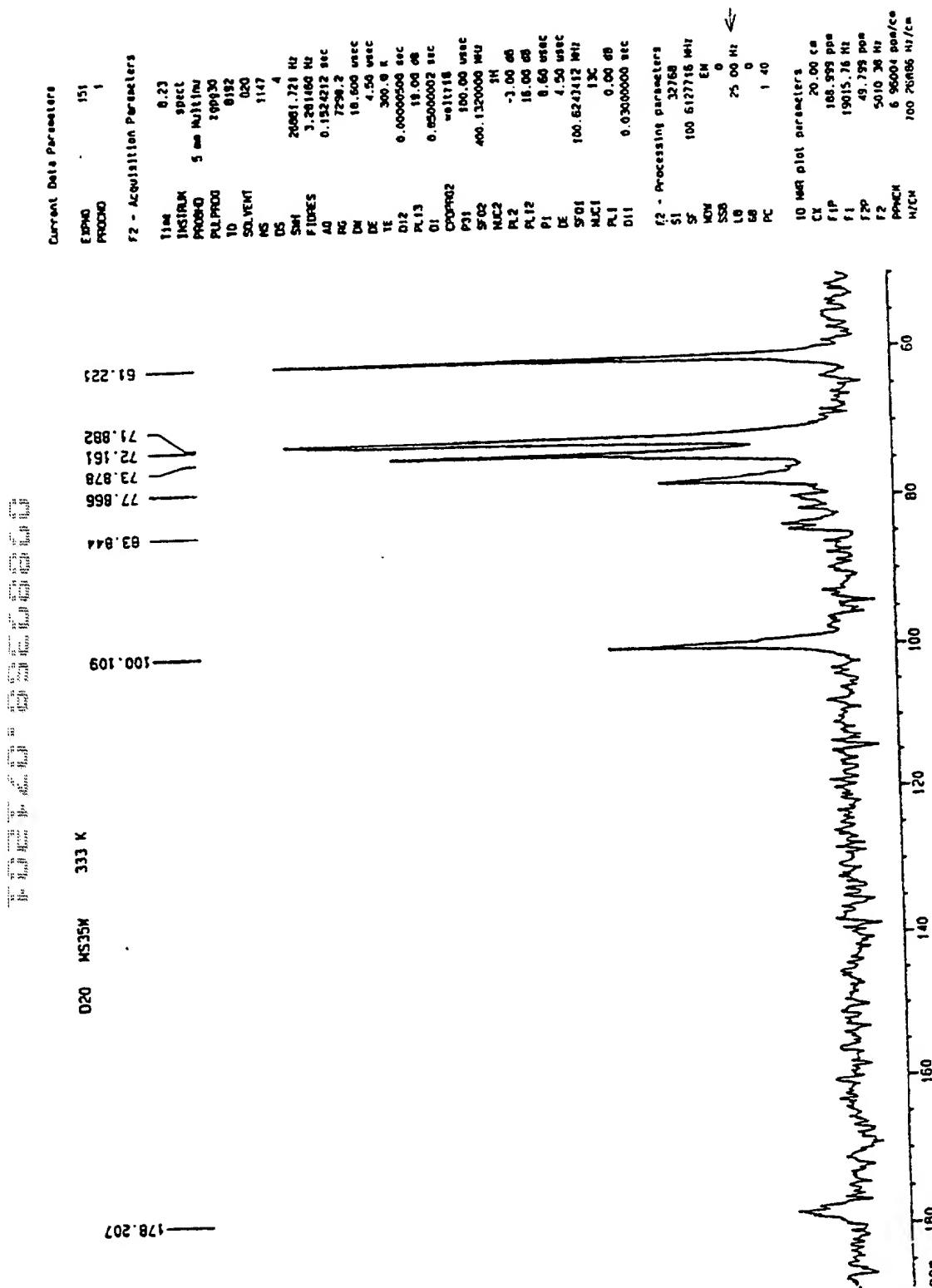
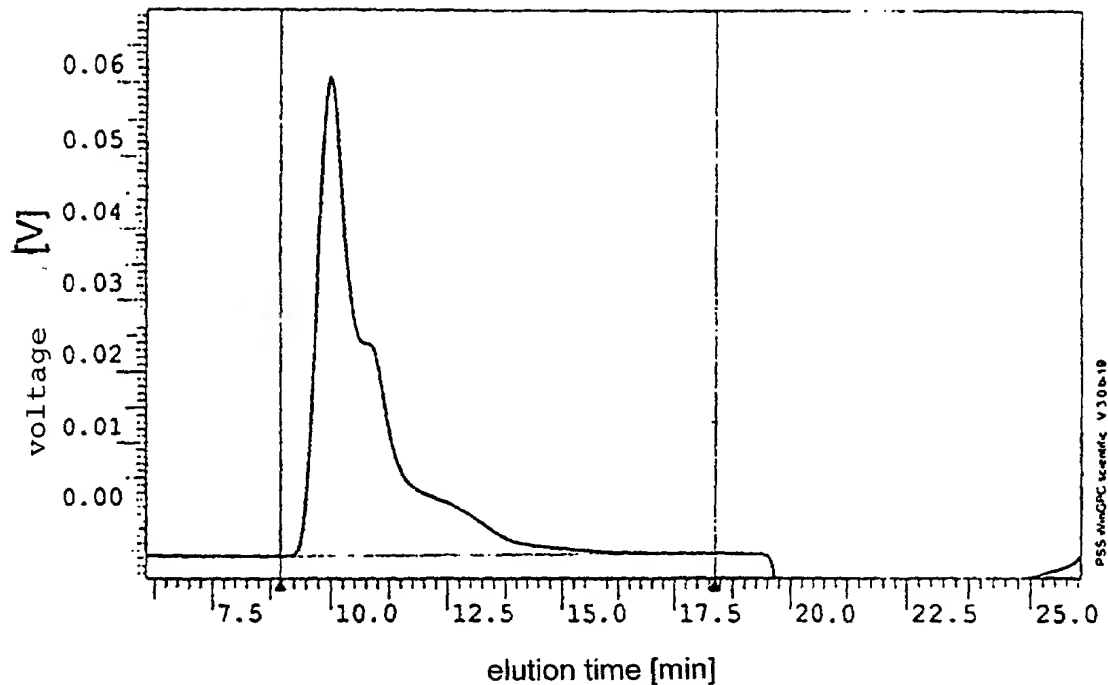


Fig. 6

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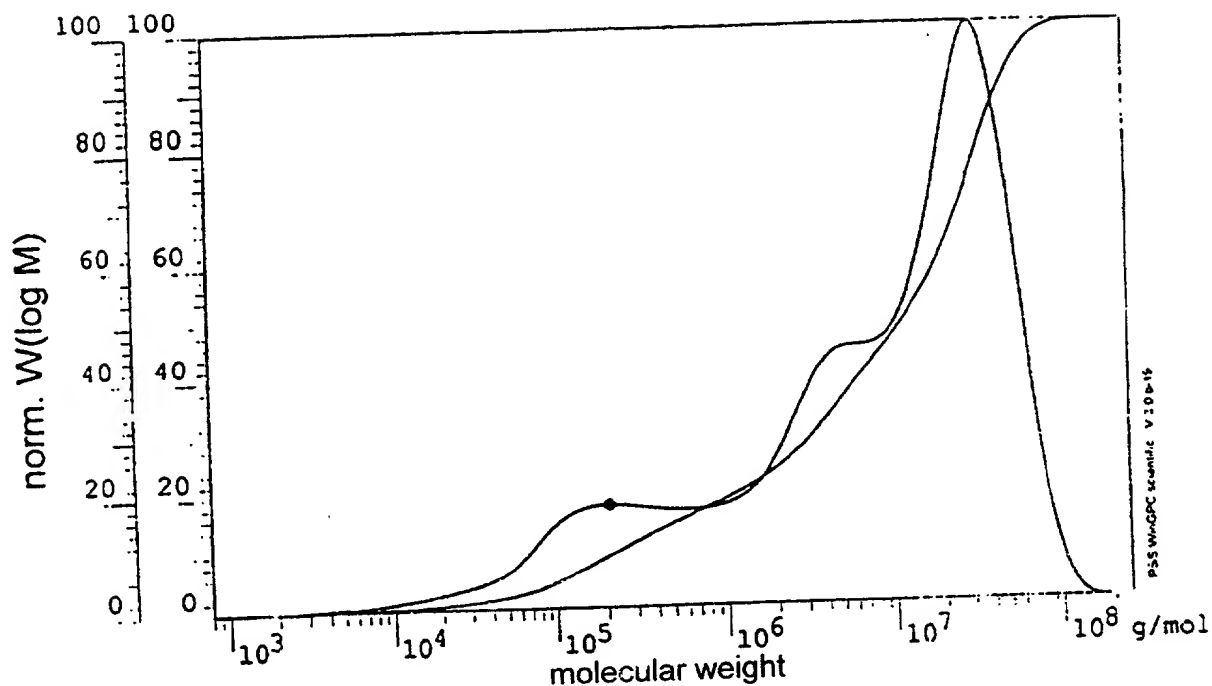


Sample:	malatyl starch/Hy		
Measured values starting:	Monday	6.054 ml	
Measured values ending:	Monday	26.054 ml	
Calibration file:	pull-no3.EIC	Eluant	twice distilled H ₂ O
minim. inhibitory concentration - A:	7.140E-01	minim. inhibitory concentration - M	1.363E-02 ml/g
Int. Standard: -E	0.000 ml	Int. Standard: -E	0.000 ml
Pump:	TSP P 100	flow rate:	1.000 ml/min
Concentration:	1.000 g/l	injection volume:	200.000 µl
Column 1:	HB 40 VOR	temperature:	
Column 2:	HB 1000	temperature:	
Column 3:	HB 40	temperature:	
Detector:	Shodex RI	displacement:	0.000 ml
Operator:		measuring intervals:	1.000 sec

Peak	Component	VP[ml]	F[V*ml]	F[%]	C[g/l]	C[%]
A:						
Sum:			0.000	100.0000	0.0000	100.0000

Fig. 7

08/10



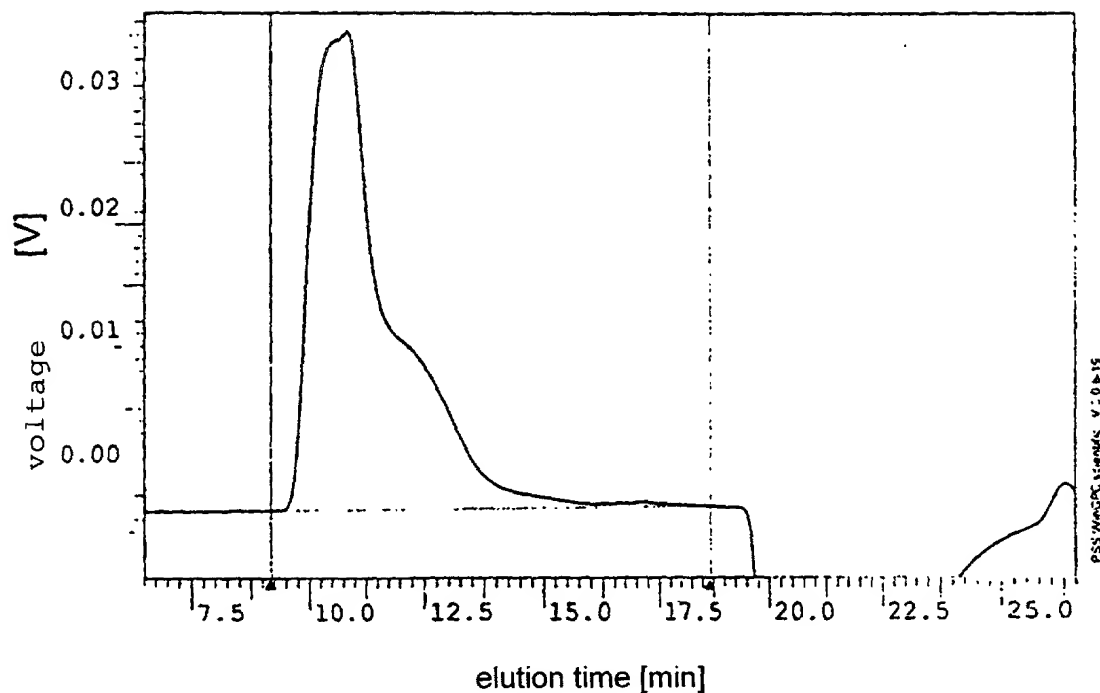
Sample:	malatyl starch/Hy	8.966 ml
Integration starting:	Monday	18.386 ml
Integration ending:	Monday	twice distilled H ₂ O
Calibration file:	pull-no3.EIC	1.363E-02 ml/g
minim. inhibitory concentration -A:	7.140E-01	0.000 ml
Int. Standard: -E	0.000 ml	1.000 ml/min
Pump:	TSP P 100	200.000 µl
Concentration:	1.000 g/l	
Column 1:	HB 40 VOR	
Column 2:	HB 1000	
Column 3:	HB 40	
Detector:	Shodex RI	0.000 ml
Operator:		1.000 sec
	Eluant	
	minim. inhibitory concentration - M	
	Int. Standard: -E	
	flow rate:	
	injection volume:	
	temperature:	
	temperature:	
	temperature:	
	displacement:	
	measuring intervals:	

Shodex RI

Mn:	4.054E+05	g/mol
Mw:	1.977E+07	g/mol
Mz:	4.307E+07	g/mol
Mv:	1.563E+07	g/mol
D:	4.877E+01	
[n]:	1.866E+03	ml/g
Vp:	1.002E+01	ml
Mp:	3.228E+07	g/mol
FI:	8.639E-02	ml*V
<450	0.00	
w%:	100.00	
>967934140	0.00	

Fig. 8

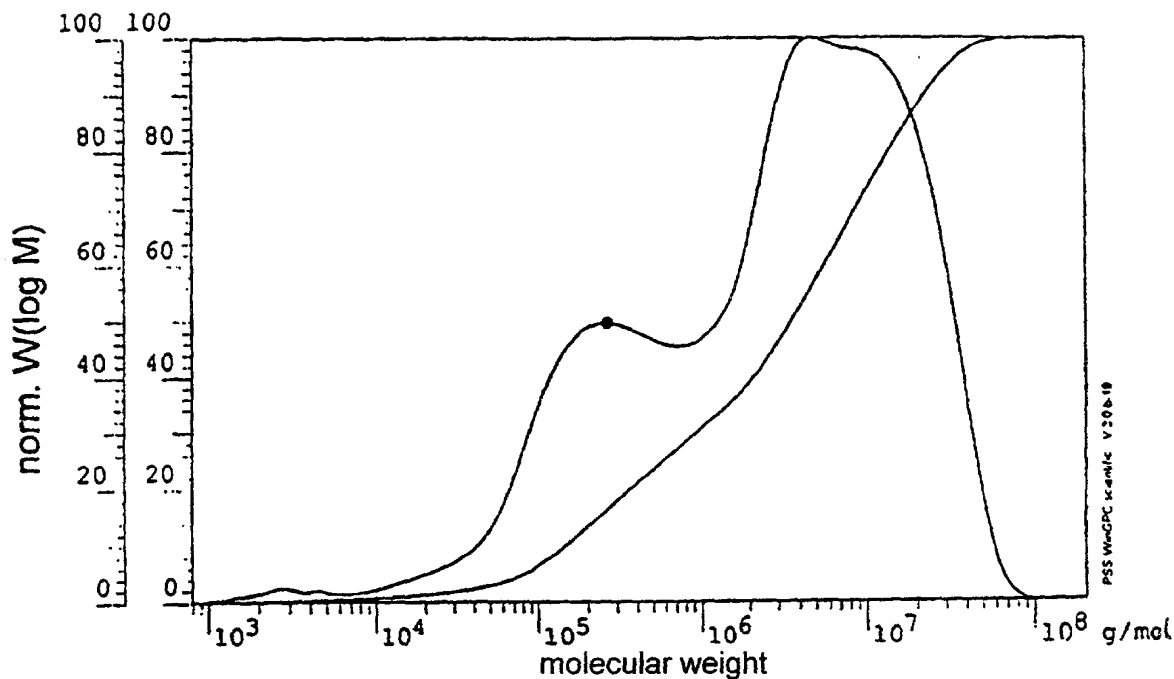
09/10



Sample:	malatyl starch/W		
Measured values starting:	Monday	6.500 ml	
Measured values ending:	Monday	26.500 ml	
Calibration file:	pull-no3.EIC	Eluant	twice distilled H ₂ O
minim. inhibitory concentration - A:	7.140E-01	minim. inhibitory concentration - K	1.363E-02 ml/g
Int. Standard: -E	0.000 ml	Int. Standard: -M	0.000 ml
Pump:	TSP P 100	flow rate:	1.000 ml/min
Concentration:	1.000 g/l	injection volume:	200.000 µl
Column 1:	HB 40 VOR	temperature:	
Column 2:	HB 1000	temperature:	
Column 3:	HB 40	temperature:	
Detector:	Shodex RI	displacement:	0.000 ml
Operator:		measuring intervals:	1.000 sec

Peak	Component	VP[ml]	F[V*ml]	F[%]	C[g/l]	C[%]
A:						
Sum:			0.000	100.0000	0.0000	100.0000

Fig. 9



Sample:	malatyl starch/W	
Integration starting:	Monday	9.189 ml
Integration ending:	Monday	18.678 ml
Calibration file:	pull-no3.EIC	Eluant
minim. inhibitory concentration -A:	7.140E-01	twice distilled H ₂ O
Int. Standard: -E	0.000 ml	minim. inhibitory concentration - K
Pump:	TSP P 100	Int. Standard: -M
Concentration:	1.000 g/l	flow rate:
Column 1:	HB 40 VOR	injection volume:
Column 2:	HB 1000	temperature:
Column 3:	HB 40	temperature:
Detector:	Shodex RI	displacement:
Operator:		measuring intervals:

Shodex RI		
Mn :	1.939E+05	g/mol
Mw :	8.100E+06	g/mol
Mz :	2.307E+07	g/mol
Mv :	6.085E+06	g/mol
D :	4.177E+01	
[n] :	9.516E+02	ml/g
Vp :	1.090E+01	ml
Mp :	4.780E+06	g/mol
FI :	7.812E-02	ml*V
<270	0.00	
w% :	100.00	
>724536690	0.00	

Fig. 10

DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION (37 CFR 1.63)

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought of the invention entitled:

MALATYL POLYSACCHARIDES, THEIR PRODUCTION AND THEIR USE

the specification of which

☐ is attached hereto, or

☒ was filed on 1/7/2000 as
US Application Ser. No. _____ or PCT Application No. PCT/DE 00/00065
and was amended on _____.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56.

I hereby claim foreign priority benefits under Title 35 U.S.C. 119 (a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(b) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or any PCT international application having a filing date before that of the application on which priority is claimed:

Prior Foreign Application Ser. No.	Country	Foreign Filing Date (Month/Day/Year)	Priority Claimed	
			Yes	No
199 00 764.0	Germany	1/12/1999	X	

I hereby claim the benefit under 35 U.S.C. 119(e) of any United States provisional application(s) listed below:

Application No.	Filing Date (Month/Day/Year)

I hereby claim the benefit under Title 35 U.S.C. 120 of any United States application(s), or 365(c) of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of 35 U.S.C. 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

U.S. Parent Application or PCT Parent No.	Parent Filing Date (Month/Day/Year)	Parent Patent No.

As a named inventor, I hereby appoint the following registered practitioner to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

GUDRUN E. HUCKETT, REGISTRATION NO. 35,747

Direct all correspondence and communications to the correspondence address and telephone and fax numbers below:

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P.O. BOX 3187
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Fax: (505) 266-2138.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

100 Full name of sole or first inventor: Dr. Waldemar Lazik

Inventor's signature [Signature]

Date: 08.07.2001

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Citizenship: Germany

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Full name of second inventor, if any:

Inventor's signature _____

Date: _____

Residence: _____

Citizenship: _____

Post Office Address: same as above

Full name of third inventor, if any:

Inventor's signature _____

Date: _____

Residence: _____

Citizenship: _____

Post Office Address: _____

Full name of fourth inventor, if any:

Inventor's signature _____

Date: _____

Residence: _____

Citizenship: _____

Post Office Address: _____

Full name of fifth inventor, if any:

Inventor's signature _____

Date: _____

Residence: _____

Citizenship: _____

Post Office Address: _____

_____ Additional Inventors are being named on the supplemental Additional Inventor(s) sheet(s)